FAST FLAMES AND DETONATIONS. John H.S. Lee. McGill University, 817 Sherbrooke St.W. Montreal, Quebec H3A 2K6.

Turbulence and adiabatic heating by shock waves are two important physical mechanisms whereby the combustion rate of a given fuel-air mixture can be increased dramatically. Apart from enhancing the energy and mass transport rates, turbulence also increases the area of the burning surface significantly. Adiabatic compression of the unburned mixture by shock waves provides an effective mechanism due to the strong exponential temperature of chemical reaction rates. The present paper describes some recent investigations of very fast turbulence flames and detonations in homogeneous fuel-air mixtures. Unlike most studies on turbulence flames where the flame is stabilized in a steady turbulent flow of unburned mixture, the present study deals with freely propagating flames where turbulence in the unburned flow ahead of the flame is induced by obstacles. Very fast flames can be generated in this manner and permits a closer look at the turbulent quenching mechanism which eventually places the upper bound on the maximum turbulent burning rate of a given system. The detonation mode of combustion exploits the shock heating mechanism to achieve the required burning rate associated with a supersonic combustion wave. The structure of detonation waves is one consisting of multiple shock intersections giving its universal cellular structure. Significant advances have been made in recent years in achieving a direct linkage between the microscopic cellular structure of the detonation front and the various macroscopic dynamic detonation properties of the mixture itself (i.e., detonability limits, initiation energy, characteristic chemical times, critical diameter, etc.).

CHEMICAL KINETIC - FLUID DYNAMIC INTERACTIONS IN DETONATIONS, E. S. Oran, Naval Research Laboratory, Code 4040, Washington D. C., 20375.

In this review we summarize the work done at the Naval Research Laboratory aimed at deciphering some of the important basic interactions occurring in detonations in gaseous mixtures. The tools for these studies have been one- and two-dimensional numerical models which couple a description of the fluid dynamics to descriptions of the detailed chemical kinetics and physical diffusion processes. Four topics will be discussed; i) the sensitivity of ignition times to perturbations in pressure or temperature [1]; ii) the structure of ignition behind shock waves and the transition to detonation [2]; iii) detailed simulations of the propagation of detonations and the structure of detonation cells [3]; iv) power-energy relations for detonation initiation [4]. We will emphasize the common factors in these topics, all of which involve a close coupling between fluid dynamics and chemical kinetics. This coupling is especially apparent in cases of weak ignition or marginal detonations.

(1) E.S. Oran and J.P. Boris Weak and Strong Ignition, II. in Combust. Flame, Nov., 1982
(2) K. Kailasanath and E. Oran, to appear Combust. Sci. Tech., 1983.
(3) E.S. Oran, T. R. Young, J.P. Boris, M.J. Picone, and D. H. Edwards, Proceedings of the 19th Symposium on Combustion, to appear 1983.
(4) K. Kailasanath, in preparation.

CHEMICAL KINETIC FACTORS IN GASEOUS DETONATIONS. C. K. Westbrook. Lawrence Livermore National Laboratory, P. O. Box 808, Livermore, California 94550.

Computer modeling techniques have been applied to study hydrogen and hydrocarbon oxidation in gaseous detonation waves. Characteristic reaction times and lengths are computed for combustible gas mixtures which have been compressed and heated by a shock wave traveling at the Chapman-Jouguet detonation velocity. These characteristic times and lengths correlate well with observed detonation parameters, including critical tube diameters for transition to spherical detonation, detonation cell sizes, critical initiation energies, and lean and rich limits for detonation in a linear tube. Detailed kinetic analysis of the structure of the induction zone in these models has been carried out and provides a great deal of new insight and information. In particular, these results show how kinetic modification of detonation parameters can occur. Inhibition or extinction of a detonation is shown to occur from increases in the ignition delay time, and increased detonability or kinetic sensitization results from decreased ignition delay times. Both processes are explained by their influence on details in the reaction mechanisms used by the numerical model.

PERTURBED OSCILLATORY REACTIONS AND EFFICIENCY OF ENGINES. John Ross. Stanford University, Department of Chemistry, Stanford, California 94305

The combustion of certain reactants ($CH_3CHO$, $C_3H_8$, isobutane) run in a well stirred continuous reactor show a variety of nonlinear properties including multiple stationary states, and simple and complex temporal oscillations of concentrations of chemical intermediates. External periodic perturbations of oscillatory reactions lead to entrainment, quasi-periodic variations, resonance responses in amplitudes, phase locking, and the possibility of a degree of control of dissipation and hence efficiency of the combustion process. We conclude with a new example of an engine which uses $\Delta G$, not $\Delta H$, of a reaction.

A REVIEW OF PLASMA JET IGNITION. R. M. Clements, Department of Physics, University of Victoria, Victoria, British Columbia, Canada, V8W 2Y2.

During the last decade or so there has been considerable interest in lean burn internal combustion engines. The motivating reasons for this are the reduction of pollutants and increased fuel economy. However such mixtures are difficult to ignite and have longer burn times by comparison to stiochiometric mixtures. One way of alleviating these problems is with plasma jet ignition. The mechanical construction of the igniter as well as the associated electrical circuitry required to power the igniter will be discussed. The igniter produces a "puff" of gas which is the ignition kernel. How this "puff" behaves will be examined when it is either in the presence or the absence of a combustable mixture. This will be done in the light of the relative roles of fluid mechanical turbulance and chemical effects. Finally the practical aspects of using these igniters in internal combustion engines and the associated problems will be reviewed.

EXPERIMENTAL AND COMPUTATIONAL STUDIES OF THE CHEMISTRY OF IGNITION PROCESSES.

Thompson M. Sloane and John W. Ratcliffe, Physical Chemistry Department, General Motors Research Laboratories, Warren, Michigan 48090

In order to explore the detailed chemistry of ignition by electric spark, plasma jet, and photochemical methods, a molecular beam mass spectrometer system for making time-resolved measurements of transient combustion phenomena has been constructed. Radicals as well as stable components of a propagating flame and of an ignition kernel have been detected. Simultaneous schlieren photographs characterize the physical processes involved in the ignition as well as the nature of the interaction of the flame with the sampling cone. These experimental results are supplemented with computational studies of idealized ignition processes. Such computations, which employ a one-dimensional model that includes detailed chemical kinetics and fluid mechanics, are helpful in understanding the chemistry of ignition processes. Our most recent experimental and computational results will be presented.

NITROGEN CHEMISTRY IN FLAMES: OBSERVATIONS AND DETAILED KINETIC MODELING.

A. M. Dean, M. S. Chou and D. Stern. Exxon Research and Engineering Company, Corporate Research-Science Laboratories, P.O. Box 45, Linden, New Jersey 07036.

Spatially resolved concentration profiles of $NH_3$, $NH_2$, NH, NO, and OH have been measured in rich ($\phi$ = 1.28-1.81) atmospheric pressure $NH_3/O_2/N_2$ flames. All species other than NO were observed via laser absorption. NO data were obtained via laser induced fluorescence and calibrated by absorption measurements in lean ammonia flames. These measurements formed the basis for an extensive series of mechanistic calculations to better define the high temperature kinetic behavior in ammonia flames. The measured NO concentrations were an order of magnitude lower at 3-4 mm above the burner than one would predict from a conventional measurement of ammonia oxidation. Furthermore, the NH, $NH_2$, and $NH_3$ concentrations were much lower than predicted. These comparisons strongly suggest that "new" reactions such as $NH_2 + NH_2$ to ultimately yield $N_2$ are important in these flames. Inclusion of these reactions yielded results in good agreement with the observations. NO profiles have also been measured in rich ($\phi$ = 1.7-1.8) atmospheric pressure $CH_4/O_2$/air flames. These NO measurements are the first to delineate the spatially resolved formation of "prompt NO". The rise and subsequent decay of the NO signal within the flame front is discussed in terms of an expanded prompt NO mechanism. The above examples illustrate the wealth of kinetic information that can be obtained by coupling laser diagnostic techniques to detailed kinetic calculations in flames. The recent advances in computational techniques and the ability to directly monitor reactive intermediates have presented kineticists with new opportunities to probe complex flame systems.

THE FORMATION OF NO AND $N_2$ FROM $NH_3$ IN FLAMES. R. J. Blint and C. J. Dasch. Physics Department, General Motors Research Laboratories, Warren, Michigan 48090.

Ammonia oxidation at high temperatures is an interesting kinetic system of significant technological importance for NO formation and destruction. Recent work has largely been devoted to the moderate temperature (1300 K) region in which $NH_3$ can quantitatively destroy NO. This paper will describe flame studies (1800- 2800 K) of $NH_3$ oxidation in which $NH_3$ is a model compound for the conversion of fuel-bound nitrogen to NO and $N_2$. A detailed (42 reactions) reaction scheme has been constructed from literature rate constants which predicts our measured flame speeds, major specie profiles, and NO levels in ammonia-oxygen-dilutent flames. These predictions require that the radical pool size and the $N_2$/NO branching be correctly described. This mechanism has been further tested against our measurements of NO emissions from $CH_4$-air flames doped with $NH_3$ and NO. This Fenimore-type "loading" experiment indicates that $NH_2$ is pivotal, but that many reaction partners (OH, O, $O_2$, $NH_2$, as well as NO) are important.

CHEMICAL KINETIC EFFECTS IN SOOT FORMATION. Irvin Glassman, Kenneth Brezinsky, Alessandro Gomez and Fumiaki Takahashi. Department of Mechanical and Aerospace Engineering, Room D-329 Engineering Quadrangle, Princeton University, Princeton, New Jersey 08544.

Evidence indicates that the fuel pyrolysis rate is the controlling factor in soot formation. Under pre-mixed flame conditions, the rate of increase with temperature of fuel pyrolysis to form the soot precursors is slower than the rate of increase of oxidation. Thus increasing the flame temperature decreases the tendency to soot. Sooting equivalence ratio data and chemical kinetic flow reactor results support this postulate and show that previous lists categorizing the tendency of fuels to soot are misleading. Recent kinetic results on the oxidation of aromatics gives great insight with regard to the aromatics propensity to soot. Since there is no oxidative attack of the fuel in a diffusion flame, sooting tendency increases with increasing flame temperature. Smoke point data as a function of temperature reveals the importance of fuel pyrolysis kinetics and initial fuel structure. Flow reactor pyrolysis kinetic results indicate that not only is the pyrolysis rate important, but also the pyrolysis intermediates formed.

SURFACE GROWTH OF SOOT PARTICLES IN PREMIXED ETHYLENE FLAMES
Stephen J. Harris and Anita M. Weiner. General Motors Research Laboratories Warren, Michigan 48090.

Most of the mass of soot particles is provided by a heterogeneous process called surface growth, in which gas phase hydrocarbon molecules (growth species) react chemically with and become incorporated into the soot particles. We have found that the greatly increased surface growth found in richer flames is accounted for primarily by the increased surface area available for growth in those flames, rather than by a higher concentration of growth species. Thus, richer flames are sootier because they have a higher nucleation rate. Depletion of the growth species does not occur in our flames. Therefore, the final mass reached by the soot particles, when surface growth has virtually ceased, is determined by a decrease in the reactivity of the soot. Our data and our analysis are consistent with surface growth being due primarily to a first order reaction of acetylene with the soot particles, diacetylene playing a minor role.

ION CONCENTRATIONS IN PREMIXED ACETYLENE FLAMES.* D.G. Keil, R.J. Gill, and D.B. Olson

A large variety of ionic species have been observed in premixed $C_2H_2/O_2$ flames. In nonsooting flames, the major ionic species are of low mass (19 or 39 amu) while in fuel rich, sooting flames, much higher ion masses are observed, in support of an ionic soot precursor mechanism. In order to evaluate the role of flame chemi-ions in the soot initiation process, we have used the electrostatic Langmuir probe technique to measure absolute total ion concentration profiles as functions of height above the burner in low pressure, laminar premixed $C_2H_2/O_2$ and $C_2H_2/O_2/M$ (M = diluent) flames with equivalence ratios, $\phi$, from considerably less than to significantly greater than the threshold equivalence ratio, $\phi_c$, where soot is first observed. The maximum flame ion concentration decreases with increasing equivalence ratio in both nonsooting and sooting flames. However, in very fuel rich sooting flames the maximum ion concentration eventually begins to increase with further flame enrichment. This phenonenon and the observed temperature effects on the ion profiles, ion concentrations, and soot threshold will be described. The implications of the observations on the ionic theory of soot formation will be discussed.

*Work supported by DOE-Pittsburgh Energy Technology Center under Contract No. DE-AC22-80PC30304 and Air Force Office of Scientific Research under Contract No. F49620-81-C-0030.

REACTIVITIES AND STRUCTURES OF $C_5H_5^+$ IONS AND THEIR RELATIONSHIP TO SOOT FORMATION. F. W. Brill, T. J. Buckley, and J. R. Eyler, Department of Chemistry, University of Florida, Gainesville, Florida 32611 and S. G. Lias and P. J. Ausloos, National Bureau of Standards, Washington, D.C. 20234.

Ion-molecule reactions have been proposed as important in the process of soot nucleation in fuel-rich flames (1). We have begun (2,3) a program of measuring the rates of ion-molecule reactions involving known flame ions and neutrals, and of using a variety of mass spectrometric techniques to determine the structures of the various isomeric ions which may be involved in these reactions. Early work concentrated on $C_3H_3^+$ ions, but studies have now been extended to $C_5H_5^+$. Several isomeric $C_5H_5^+$ ions can be formed by electron impact on neutral precursors, and we have determined their ion-molecule reaction rate constants with a number of neutrals found in flames, and have carried out both experimental and theoretical studies to help determine which of many possible structures should be assigned to each isomer. Structure and reactivity results will be presented and their relevance to ionic soot formation mechanisms discussed.

1. H.F. Calcote, Combustion and Flame 42, 215 (1981).

2. P.J. Ausloos and S.G. Lias, J. Amer. Chem. Soc. 103, 6505 (1981).

3. F.W. Brill and J.R. Eyler, J. Phys. Chem. 85, 1091 (1981).

THE DEPENDENCE OF SOOT YIELD ON FLAME CONDITIONS -- A UNIFYING PICTURE.
Howard S. Homan, Exxon Research and Engineering Company, P. O. Box 51, Linden, NJ 07036.

A plot is presented which summarizes the trends of soot yield as a function of flame temperature and equivalence ratio for both premixed flames and diffusion flames. Schematic contours of soot yield are drawn to represent trends induced from published data. For underventilated diffusion flames, the increase in soot yield with increasing flame temperature and with addition of small amounts of oxygen to the fuel side are represented. For premixed flames, the increase in soot yield with increasing equivalence ratio and the decrease in soot yield with increasing flame temperature are represented. For overventilated diffusion flames, the soot yield is a function of heterogeneous post-flame oxidation which is discussed separately from the plot. For reference, calculated values of adiabatic flame temperature versus equivalence ratio are included. A hypothetical laboratory burner experiment -- a consolidation of experiments cited in the literature -- is presented to show how the plot unifies much phenomenological data on soot formation. Armed with this summary, a researcher should be better able to interpret the complex changes of soot yield with operating conditions of practical devices.

KINETICS OF COAL PARTICLE GASIFICATION.*
T.G. DiGiuseppe, S. Madronich, and W. Felder, AeroChem Research Laboratories, Inc., P.O. Box 12, Princeton, NJ 08540

An understanding of the chemical and physical processes of coal gasification may be obtained through a detailed study of the kinetics of volatile reaction products released during pyrolysis of coal particles. We have recently begun a systematic investigation of the chemical transformations occurring during the gasification of coal particles, using AeroChem's High Temperature Fast Flow Reactor (HTFFR). Freshly prepared sized coal particles are entrained into the HTFFR through a fluidized bed and are pyrolyzed under controlled conditions of temperature, pressure, and gas flow velocity. Kinetic and mechanistic information is obtained by real time detection of the primary products of the pyrolyzing coal. In our initial experiments, gas chromatography has been used for the detection of carbon monoxide, methane, water, and carbon dioxide. Quantitative measurements of the concentrations of these species have been obtained for 100 μm diam coal particles pyrolyzing at temperatures from 1000 K to 1300 K at pressures to 50 Torr, and residence times from 0.5 to 1.5 s. Gas chromatographic and mass spectrometric techniques are currently being used for the quantitative detection of hydrocarbon products. These results will be applied to the development of basic quantitative models of the coal gasification process.

*Work supported by the Gas Research Institute under Contract No. 5081-360-0531.

THEORETICAL INVESTIGATIONS OF REACTION PATHWAYS FOR THE OXIDATION OF NH AND $NH_2$ RADICALS.* C. F. Melius and J. S. Binkley. Sandia National Laboratories, Livermore California 94550.

Reaction intermediates and possible products for the reactions of the NH and $NH_2$ radicals with O, $O_2$ and NO have been investigated using the recently developed BAC-MP4 method (bond-additivity corrections applied to fourth-order Møller-Plesset perturbation theory). Stationary-point geometries have been calculated for stable minima and selected transition structure species using a split-valence polarized basis at the Hartree-Fock level. Using these geometries zero-point vibrational corrections and fourth-order perturbation theory total energies are combined with the bond-additivity corrections to obtain final total energies. In those cases where transition structure calculations have not been performed, estimates of the barriers are made. These results are used to predict likely pathways for reactions of these species occurring under various temperature and pressure conditions. Our results are compared with available experimental data and with various chemical kinetics models used in combustion.

*This work was supported by the U.S. Dept. of Energy.

LASER PHOTOLYSIS/LASER-INDUCED FLUORESCENCE KINETIC STUDIES OF ELEMENTARY COMBUSTION REACTIONS.* Frank P. Tully, Applied Physics Division, Sandia National Laboratories, Livermore, CA 94550.

A new, laser-based, chemical kinetics technique has been demonstrated in studies of the reactions of the hydroxyl radical with prototype hydrocarbon fuel molecules. Following reaction initiation by excimer laser photolysis, time-resolved OH concentration profiles were measured with a highly sensitive, quasi-cw, laser-induced fluorescence method The visible output of a synchronously pumped dye laser, a train of pulses of 3-6 nJ energy and 8-10 ps duration at a repetition rate of 246 MHz, has been frequency-doubled using temperature- and angle-tuned SHG crystals. More than 50 mW of quasi-cw, tunable ultraviolet, laser radiation has been generated. OH fluorescence was excited at 308.16 nm, and OH decay profiles, characterized by at least one order of magnitude improvement in S/B over those obtainable with resonance lamp detection, were collected as functions of gas mixture composition. Absolute reaction rate coefficients were measured over the temperature and pressure ranges 291-1000 K and 50-600 Torr, respectively. Mechanistic information was obtained directly from the OH decays and as a result of deuterium substitution in reactants. For example, in the reaction between hydroxyl radicals and ethylene, the mechanism is dominated at low temperatures by electrophilic addition of OH to the double bond, and, as the temperature is raised, by increasingly rapid decomposition of the thermalized adduct $HOC_2H_4$ back to reactants. The current status of experiments utilizing this powerful technique will be discussed.

*This work was supported by the U.S. Department of Energy.

LASER PYROLYSIS/LASER FLUORESCENCE MEASUREMENT OF THE OH + $C_2H_2$ REACTION RATE NEAR 1200 K*. Paul W. Fairchild, Gregory P. Smith, and David R. Crosley. SRI International, Menlo Park, California 94025.

A laser pyrolysis/laser fluorescence apparatus has been used to measure the rate constant for the reaction of hydroxyl radicals with acetylene at temperatures near 1200 K. A mixture of $SF_6$, $N_2$ and $H_2O_2$ was irradiated with a pulsed $CO_2$ laser, causing rapid heating and pyrolyzing the peroxide to form OH radicals. The OH concentration is then measured using fluorescence from electronically excited OH. This is produced by a frequency doubled dye laser, fired after a variable time delay following the $CO_2$ laser. Addition of $C_2H_2$ causes a decrease in the OH signal with time, premitting a measurement of the rate constant. Experiments were performed at a total pressure of 40 torr and a temperature of 1160 ± 50 K as determined by rotational excitation scans in the OH. A value of $4 \times 10^{-13} cm^3/sec$ was determined for these conditions; measurements extending the range of temperature and pressure are in progress.

*Supported by the Department of Energy under Contract DE-AC03-81ER10906.

MEASUREMENT OF THE $C_2$ ($a^3\Pi_u$) DISAPPEARANCE RATES WITH $O_2$ IN THE 298 - 1300 K TEMPERATURE RANGE. Steven L. Baughcum and Richard C. Oldenborg, University of California, Los Alamos National Laboratory, Chemistry Division, Los Alamos, New Mexico, 87545.

The disappearance rates of $C_2$ ($a^3\Pi_u$) (v=0, v=1, and v=2) in the presence of $O_2$ have been measured over the 298-1300 K temperature range. The $C_2$ is produced by 2-photon dissociation of $CF_3CCCF_3$ at 193 nm and probed by laser-induced fluorescence tuned to the $d(^3\Pi_g) \leftarrow a(^3\Pi_u)$ transition. The disappearance rate of $C_2$ ($a^3\Pi_u$) (v=0) as a function of temperature is fit extremely well by the Arrhenius expression ($k(T) = A \exp(-E/RT)$) with a barrier of 0.97 kcal/mole. The quality of the fit over such a large temperature range provides a test of previously proposed models of the $C_2 + O_2$ system, which do not predict simple Arrhenius behavior. Our results are consistent with a model in which the equilibration rate between $C_2$ ($a^3\Pi_u$) and $C_2$ ($X\ ^1\Sigma_g^+$) in the presence of $O_2$ is the rate limiting step, rather than the reaction rate. The measured-barrier height of 0.97 kcal/mole is then the barrier for intersystem crossing in the $^3C_2 + O_2 \rightarrow {}^1C_2 + O_2$ reaction. Additional experiments on $C_2$ ($X\ ^1\Sigma_g^+$) kinetics will be presented.

REACTION OF $C_2H$ WITH $O_2$: RATE CONSTANT FOR CO FORMATION. A. H. LAUFER and R. LECHLEIDER, National Bureau of Standards, Chemical Kinetics Division, Center for Chemical Physics, Washinton, DC 20234.

The rate constant for CO production from the reaction of $C_2H$ with $O_2$ has been investigated using flash photolysis of a suitable $C_2H$ precursor in conjunction with analysis of CO by absorption in the vacuum ultraviolet. $C_2H$ concentrations were determined by titration with added alkanes followed by gas chromatographic analysis of product $C_2H_2$. The rate constant was determined to be $4.0 \pm 0.5 \times 10^{-12} cm^3 molec^{-1} s^{-1}$. The CO increase is best explained as originating from two primary reaction channels

a) $C_2H + O_2 = C_2HO + O$

b) $C_2H + O_2 = CO + HCO$

The best fit to the data suggests that (a) represents 20% of the total process. The relationship of the $C_2H + O_2$ rate constant to those for reaction of $C_2H$ with hydrocarbons will be discussed.

REACTION OF CARBON MONOXIDE WITH OXYGEN ATOMS PRODUCED IN THE THERMAL DECOMPOSITION OF OZONE, S. Toby, S. Sheth, F.S. Toby, Dept. of Chemistry, Rutgers University, Piscataway, NJ 08854

The reaction of CO with $O_3$ has been reinvestigated in the range 80-160°C and it was shown that the previously reported[1] complex rate law occurs as the result of a chain reaction initiated by trace impurities in the CO. This conclusion was also in accord with a computer simulation of the system. When the CO was rigorously purified[2] the reaction reduced to the sequence $O_3 + CO \xrightarrow{1} O(^3P) + O_2 + CO$, $O(^3P) + O_3 \xrightarrow{2} 2O_2$ followed by reactions of $O(^3P)$ with CO. These reactions lead to chemiluminescence and by measuring the emitted intensity we measured $k_4/k_2$ for $O(^3P) + CO \xrightarrow{4} CO_2(^3B_2)$. The rates of reactions 4 and 2 were found to have the same temperature dependence in the range studied. There was no third body effect on reaction 4 which is in agreement with the mechanism postulated by Pravilov and Smirnova[3].

1. S. Toby and E. Ullrich, Int. J. Chem. Kins., 12, 535 (1980).
2. D.H. Stedman, D.K. Branch and R. Pearson, Anal. Chem., 51, 2340 (1979).
3. A.M. Pravilov and L.G. Smirnova, Kinetika i Kataliz, 22, 832 (1981).